PHOTOCATALYTIC DEGRADATION OF PHENOL IN AQUEOUS SOLUTION USING Fe/TiO_2 THIN FILMS UNDER UV AND VISIBLE LIGHT.

by

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Thesis submitted in fulfillment of the requirements for the degree of Master of Science

JANUARY 2008

ACKNOWLEDGEMENTS

Syukur, alhamdulillah to Allah SWT for the completion of this study.

First of all, I would like to express my deepest gratitude to my supervisor, Prof. Abdul Rahman Mohamed for his guidance and assistance throughout my study. He had also shown compassion and concern to me through my pregnancy, my child's health complications and my ectopic pregnancy complications. Thank you for understanding my problems and for the encouragements given. I would also like to extend my appreciation to Prof. Subhash Bhatia for his time, advice and valuable input regarding my work. I am also taking this opportunity to humbly apologize to both of them for any inconvenience I have unintentionally caused them.

I am thankful to the Dean, Prof. Abdul Latif Ahmad and the Deputy Deans, Dr. Mashitah Mat Don and Dr. Syamsul Rizal Abd Syukor for their support and assistance towards making this research a success. Not forgetting all the respective lecturers, staff and technicians of School of Chemical Engineering, thank you for the help given, either directly or indirectly. A special thank you goes to En. Mohd. Faiza Ismail and Pn. Latifah Latif for their technical assistance in the laboratory. Additionally, I am grateful to En. Wahab (Glass Workshop, School of Chemical Science) and the technicians of School of Material and Mineral Resources Engineering and School of Biological Science for the help with sample analyses.

To my parents, Hj. Mansor Ali and Hjh. Kemariah Halim, I can never fully repay their love and endless support. They kept me going even when I was ready to give up. I am deeply indebted to them and I truly wish that I have made them proud. To my beloved husband, Yusuf Zakaria and my son, Shahrin, thank you for being there for me. I love you both. Finally, to all my friends, especially Zulfakar, your contributions are very much appreciated and the wonderful time I've spent with all of you will be remembered always.

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Symbol	Description	Unit
C_p	Phenol concentration at time t	ppm
C_{po}	Initial phenol concentration	ppm
dC_p/dt	Differential of C_p polynomial with respect to t	ppm/min
e^-	Photon generated electron on the photocatalyst	-
h^+	Photon generated hole on the photocatalyst	-
k	Reaction rate constant	ppm/min
K	Adsorption equilibrium constant	1/ppm
k_{app}	Apparent rate constant	min^{-1}
OH^-	Hydroxide ion	-
$OH^\bullet$	Hydroxyl radical	-
P_{ads}	Adsorbed organic pollutant	-
pH_{pzc}	Point of zero charge	-
R^2	Correlation coefficient	-
$(-r)_p$	Reaction rate	ppm/g.min
$(-r_p)_o$	Initial rate of reaction for phenol degradation	ppm/min
t	Time	min
V	Volume of treated phenol solution	L
W_{est}	Estimated weight per coated surface area	g/cm^2

Greek Symbols

λ	Wavelength of the UV lamp	nm
α	Alpha (axial distance from the center point which makes the design rotatable)	-
Θ	Surface coverage	-

LIST OF ABBREVIATIONS

ANOVA	Analysis of variances
AOP	Advanced oxidation processes
BOD_5	Biochemical oxygen demand
CCD	Central composite design
CdS	Cadmium sulfide
Co	Cobalt
CO_2	Carbon dioxide
Cr	Chromium
CVD	Chemical vapor deposition
DEA	Diethanolamine
DOE	Design of experiments
EDX	Energy dispersive X-ray spectroscopy
EPA	Environment Protection Agency
Fe	Iron
Fe_2O_3	Iron (III) oxide
Fe/TiO_2	Fe-doped titanium dioxide immobilized on support
GAC	Granular activated carbon
HCl	Hydrochloric acid
HPLC	High performance liquid chromatography
H_2O	Water
H_2O_2	Hydrogen peroxide
i-PrOH	Isopropanol
MB	Methylene blue
Mn	Manganese
MSDS	Material safety data sheet

NaOH	Sodium hydroxide
Ni	Nickel
O_2	Oxygen
$OH^{\bullet}$	Hydroxyl radicals
OSHA	Occupational Safety and Health Administration
PBT	Persistent, bio-accumulative and toxic
PEL	Permissible exposure limit
rpm	Rotation per minute
RSM	Response surface methodology
SEM	Scanning electron microscopy
TiO_2	Titanium dioxide
TTIP	Titanium (IV) isopropoxide
UV-A	365 nm ultra-violet wavelength
UV-C	254 nm ultra-violet wavelength
V	Vanadium
VOCs	Volatile organic compounds
XPS	X-Ray photoelectron spectroscopy
XRD	X-Ray diffraction
ZnO	Zink oxide
2-ClA	2-Chloroanaline

PENURUNAN FENOL BERFOTOMANGKIN DALAM LARUTAN BERAIR MENGGUNAKAN SAPUT NIPIS Fe/TiO_2 DI BAWAH CAHAYA ULTRAUNGU DAN CAHAYA NAMPAK.

ABSTRAK

Penurunan fenol berfotomangkin melalui pengoksidaan, dengan menggunakan TiO_2 terdop (Fe/TiO_2) sebagai fotomangkin dalam bentuk saput nipis tersekat gerak di dalam sebuah reaktor penurunan kelompok berjaket adalah subjek kajian ini. Fotomangkin Fe/TiO_2 telah berjaya disintesis dengan menggunakan kaedah sol gel dan disalut ke atas substratum kaca terpilih dengan menggunakan kaedah salutan basah iaitu salutan-celup. Titanium isopropoksida telah digunakan sebagai prapenanda titanium, isopropanol sebagai pelarut dan dietanolamin (DEA) sebagai agen penstabilan. Penambahan ion logam peralihan, Fe telah digunakan sebagai bahan dop untuk penyediaan saput nipis TiO_2. Tujuan penambahan bahan dop ini ialah untuk memulakan anjakan merah dalam spektrum penyerapan fotomangkin TiO_2 untuk kegunaan dalam cahaya nampak. Ciri-ciri saput nipis tersalut ini telah ditentukan dengan corak XRD, yang menunjukkan fasa-fasa berhablur anatis dan rutil. Fasa berhablur Fe juga telah dikesan pada $2\theta = 48.1^{\circ}$. Imej SEM telah menunjukkan bahawa permukaan substratum telah disaluti dengan sepenuhnya dengan saput nipis dengan rekatan yang baik. Spektrum EDX untuk saput Fe/TiO_2 telah mengesan kewujudan titanium dan besi (Fe) dalam saput tersebut. Dalam kajian ini, prestasi TiO_2 yang telah disintesis telah dikaji untuk penurunan fenol di dalam reaktor pemfotomangkinan. Nilai-nilai optimum untuk pembolehubah proses yang dikaji adalah; kepekatan awal fenol pada 50 ppm, bebanan mangkin Fe/TiO_2 pada 3 lapisan, pH larutan pada pH 3 dan kepekatan H_2O_2 pada 300 ppm. Untuk kajian kesan panjang gelombang, Fe/TiO_2 telah menunjukkan aktiviti tertinggi dalam cahaya ultraungu, dengan menurunkan 87.3 % fenol dalam masa 6 jam. Ia telah berjaya menurunkan 37.0 % fenol walaupun di bawah penyinaran cahaya nampak. Model kinetik Langmuir-Hinshelwood yang diterima pakai dengan meluas telah digunakan untuk kinetik

tindakbalas di dalam kajian ini. Penurunan fenol dalam kajian ini telah didapati padan dengan kinetik tertib pertama. Nilai pemalar kadar yang telah diperoleh adalah k = 0.325 ppm/min dan nilai pemalar jerapan adalah K = 0.153 1/ppm. Perisian rekabentuk eksperimen (DOE) juga telah digunakan. Keadaan optimum untuk penurunan fenol sebagaimana yang dicadangkan oleh rekabentuk tersebut adalah pada 50 ppm kepekatan awal fenol, pada pH 5 dengan 100 ppm H_2O_2.

PHOTOCATALYTIC DEGRADATION OF PHENOL IN AQUEOUS SOLUTION USING Fe/TiO_2 THIN FILMS UNDER UV AND VISIBLE LIGHT

ABSTRACT

Photocatalytic degradation of phenol by oxidation, utilizing doped TiO_2 (Fe/TiO_2) as photocatalyst in the form of immobilized thin films in a jacketed photocatalytic batch reactor was the subject of this research. Fe/TiO_2 photocatalyst was successfully synthesized using sol-gel method and coated on the chosen glass substrates using the wet coating method of dip-coating. Titanium isopropoxide was used as the titanium precursor, isopropanol as the solvent and diethanolamine (DEA) as the stabilizing agent. The addition of transition metal ion, Fe was utilized as the dopant for the preparation of TiO_2 thin films. The purpose of adding this dopant is to initiate the red shift in the absorbance spectrum of TiO_2 photocatalyst for usage in visible light. The characteristics of the coated thin films were determined by XRD patterns, showing anatase and rutile crystalline phases. Fe crystalline phase was also detected at 2θ = 48.1°. SEM images showed that the surface of the supports was completely covered with thin film with good adhesion. EDX spectrum for Fe/TiO_2 films detected the existence of titanium and iron (Fe) within the films. In this research, the performance of the synthesized TiO_2 was studied for the degradation of phenol in a photocatalytic reactor. The optimum values for the studied process variables were; initial phenol concentration of 50 ppm, Fe/TiO_2 catalyst loading of 3 layers, solution pH at pH 3 and H_2O_2 concentration of 300 ppm. For the study on the effect of wavelength, Fe/TiO_2 showed the highest activity in UV light, able to degrade 87.3 % phenol in 6 hours. It successfully degraded 37.0 % phenol even under visible light irradiation. The widely accepted Langmuir-Hinshelwood kinetic model was used for the reaction kinetics in this study. The degradation of phenol in this study was found to fit the first order kinetics. The obtained rate constant was k = 0.325 ppm/min while the adsorption constant was

K = 0.153 1/ppm. The Design of Experiments (DOE) software was also utilized. The optimum conditions for phenol degradation as proposed by the design were 50 ppm initial phenol concentration, at pH 5 with 100 ppm H_2O_2.

CHAPTER ONE

INTRODUCTION

1.1 WATER TREATMENT

Physical unit operations, chemical and biological unit processes are the main water treatment methods. Their main concerns are to remove suspended and floatable materials, to treat biodegradable organic and to eliminate any pathogenic organisms. Preliminary treatment is the first treatment stage and it refers to physical unit operations, which are applied to any wastewater treatment system. In this stage, any materials in wastewater are removed through the screening and grinding/pulverizing process for suspended solids and other organic matter. The sedimentation process is used for grit removal and flotation process is for excess oil and grease removal.

Secondary treatment refers to chemical and biological unit processes, where the targets are biodegradable organic and any remaining suspended solids. Biological unit processes remove pollutants by biological activity (aerobic and anaerobic cycles). The chemical unit processes however apply the use of chemicals or by chemical reactions. These include precipitation, adsorption and disinfection. Tertiary treatment refers to a combination of all the three processes because it removes nutrients, toxic substances including heavy metals and further removal of suspended solids and organic matter.

Unfortunately, as reported by Indah Water Consortium Sdn. Bhd., these methods can only partially treat wastewater. At the end of the day, the treated wastewater is discharged as an effluent still rich in organic material. For example, colored dye effluents which contain significant level of toxic organic contaminants. These substances are often resistant to degradation by biological methods and are not

removed effectively by conventional physio-chemical treatment methods (Ravikumar *et al*., 2007). It is during the tertiary treatment that heterogeneous photocatalysis can be applied to completely remove contaminants/pollutants existing in the treated effluent.

1.2 HETEROGENEOUS PHOTOCATALYSIS

Heterogeneous photocatalysis has become an increasingly viable technology in environmental remediation. Photocatalytic degradation utilizing titanium dioxide (TiO_2) as photocatalyst has several advantages with comparison to traditional water purifications and wastewater treatment methods. Complete destruction of most contaminants without the hassle of disposing spent catalyst/adsorbent is one of them. Photocatalysis also runs at room temperature and pressure, and the photocatalyst is very stable with high efficiency when activated using ultraviolet light (λ < 380 nm) (Adan *et al.,* 2007). The widely used TiO_2 is reported to be photochemically stable, non-toxic and inexpensive (Sakthivel *et al*., 2002; Silva *et al.,* 2007).

A photocatalytic process usually requires these basic elements; a semiconductor or photocatalyst, a light source, a reactor system and the pollutant. According to Ray and Beenackers (1998), ultraviolet energy produces photons that will be absorbed by the photocatalyst, thus activating it. Its activation is preceded by the formation of pairs of electrical charges-holes in the valence band and electrons in the conductivity band. It has been reported that these holes will react with water molecules, forming hydroxyl radicals, which are strong oxidants of the organic molecules (Trapalis *et al*., 2003).

Most of the photocatalyst systems reported in the literature employ two types of TiO_2. Mostly, researchers used commercial TiO_2 fine powders such as Degussa P25 (Degussa, Germany), Aldrich (Sigma Aldrich, Germany) and Hombikat UV100 (Sachtleben Chemie, Germany). There are also those who synthesize their own TiO_2

through sol-gel or by adding TiO_2 fine powders to sol solutions to produce anchored or more commonly known as, immobilized TiO_2. Unfortunately, problems do occur in both uses of TiO_2 fine powders and anchored TiO_2. Basically, it is difficult to recover TiO_2 fine powders after the reactions while the activity becomes low due to the diminution of surface area by anchoring TiO_2 fine powders or sol-gel onto supports (Yu *et al*., 2000).

1.3 PROBLEM STATEMENT

Utilizing titanium dioxide as photocatalyst has one disadvantage whereby its bandgap energy of 3.2 eV requires UV illumination to activate it. TiO_2 only absorbs about 3 – 5 % energy of the solar spectrum (400 – 800 nm) (Anpo, 2000; Sonawane *et al*., 2004). Therefore, this absorption edge needs to be extended to the visible range if the photocatalyst is to be used in applications, which involve direct sunlight. Thus, bandgap narrowing by using transition metal ions as dopants is one of the most appropriate methods to be used in achieving this goal.

In the present study, the focus is on developing immobilized thin films of doped TiO_2 for use in photocatalysis. The intention is to shift the absorption bandgap energy of the synthesized TiO_2 thin film towards visible light spectrum by adding a dopant. Investigated dopants showing such a shift could be observed with Cr, V, Fe, Ni, Mn and Co (Jin and Shiraishi, 2004). In this study, ferric nitrate will be used as the doping material. It was recorded that doping Fe^{3+} to TiO_2 had generated an additional energy level within the bandgap of the catalyst, making it possible for electron excitation with visible light, also known as the red shift, to happen (Kim *et al*., 2004). Others had also documented that the increase in catalytic activities of doped TiO_2 is due to the shift in optical absorption in the visible region and also to the lowered catalyst's bandgap value (Brezova *et al*., 1997; Trapalis *et al*., 2003; Sonawane *et al*., 2004). Fe^{3+} dopant in TiO_2 can also act as electron/hole trappers, thus reducing the recombination rate of the electron/holes (Yang *et al*., 2002; Nahar *et al.,* 2006).

Apart from that, the aim to immobilize TiO_2 sol gel is as a solution to the limitation in the use of photocatalyst powder. Ray and Beenackers (1998) reported that in photocatalytic systems with suspended or slurry TiO_2, the separation of the catalyst from the solution can be an inconvenient and time consuming process. The separation process for suspended TiO_2 in large scale technical application in wastewater treatment is also unsuitable and would lead to an increase in the start-up cost (Blazkova *et al*., 1998; Grzechulska and Morawski, 2003). Furthermore, suspended TiO_2 particles have been reported to aggregate at high photocatalyst loading (Lee *et al*., 2003). In such situation, the depth of UV light penetration into the solution is limited. This could be due to strong absorption by the photocatalyst particles and the dissolved organic pollutant (Ray and Beenackers, 1998). The above problems can be avoided by immobilizing the photocatalyst on a suitable support in such a way as to provide high surface area and accessibility of the catalyst.

1.4 RESEARCH OBJECTIVES

The main goal of this study is to develop an improved TiO_2 thin film photocatalyst for repeated usage without significant attrition of the immobilized films and to lower the photocatalyst's bandgap energy for the utilization of visible light with elevated UV activity. The objectives of this study are:

i) To synthesize immobilized doped TiO_2 photocatalyst on quartz and Pyrex glass tubes using the sol gel method.

ii) To characterize the immobilized TiO_2 thin films using XRD, EDX and SEM.

iii) To study the effect of important operating variables; solution pH, initial phenol concentration, photocatalyst loading and H_2O_2 concentration on the degradation of phenol in the jacketed photocatalytic batch reactor.

v) To determine the relevant reaction kinetic parameters from the Langmuir-Hinshelwood kinetic model representing the degradation rate of phenol over different concentrations.

vi) To obtain optimum process variables for phenol degradation using Design of Experiment.

1.5 RESEARCH SCOPE

This research is focused on immobilizing TiO_2 on a suitable support while altering its bandgap energy to the visible range for activation by solar energy. The development of the photocatalyst includes studying the effect the chosen dopant, ferric nitrate, has on the activity of TiO_2 thin films.

Characterization of the doped thin film (Fe/TiO_2 thin film) was carried out using analytical instruments which include the scanning electron microscopy (SEM), energy dispersive X-Ray spectroscopy (EDX) and X-Ray diffraction (XRD). The degradation performance and activity of this chosen system has also been studied and recorded. In this study, the process variables investigated includes the effect of photocatalyst loading (1 layer, 3 layers and 5 layers of Fe/TiO_2 thin films), the effect of initial phenol concentration (10 – 500 ppm), the effect of solution pH (pH 3 – pH 11) and the effect of hydrogen peroxide (H_2O_2) concentration (50 – 300 ppm). The dependence of phenol degradation using Fe/TiO_2 films on different irradiation wavelength (254 nm, 365 nm and visible light) was also studied. Each variable were chosen based on reports in the literature and through the process of trial and error. Finally, these results were employed for a kinetic study based on Langmuir-Hinshelwood equation.

The Design of Experiment (DOE) using the Design-Expert (version 6.0.6, StatEase, Inc., USA) was employed to obtain the optimum value of three process variables for the degradation of phenol. The selected variables were the initial phenol concentration (50 – 100 ppm), solution pH (pH 3 – pH 5) and initial H_2O_2 concentration (100 – 300 ppm).

1.6 ORGANIZATION OF THESIS

This thesis is made up of five chapters that cover important details regarding this research.

This first chapter includes a brief introduction on water treatment and the role of heterogeneous photocatalysis. The problem statement gives the problems the present research is aimed to study. This is followed by the objectives of the study. The research scope states the overall characterization, experiments and analysis conducted throughout the research.

Chapter Two consists of the literature review conducted on photocatalysis researches. A brief introduction about phenol is introduced in the first part, followed by the overview about photocatalysis. The importance of reactor configuration is also included as it plays a big role wherein the reaction takes place. Then, information regarding titanium dioxide (TiO_2), the photocatalyst makes up the second part of this chapter. In this part, previous works regarding synthesizing, doping and immobilizing TiO_2 on supports are recorded in relevance to the current research. The third part is all about the effects of the various operating variables have on the performance of the photocatalyst for the degradation of phenol. The final part is an overview of the design of experiments (DOE) introducing the response surface methodology (RSM) applied in this study. It was used to obtain the optimum value of three chosen variables in the degradation of phenol.

In Chapter Three, all the experimental work has been listed and explained in details. The first part consists of all the physical and chemical data for each chemicals used during the experiments, shown in tables for easy identification. A thorough description of the annular photocatalytic batch reactor comes next, complete with a set of pictures for better understanding of the whole set-up. In the second part, three preparation methods used to develop the photocatalyst were recorded. The first step was to pre-treat the supports; Pyrex and quartz glass tubes, to be coated with doped TiO_2 sol gel. As for the preparation of the TiO_2 sol-gel, it was based on the work of Balasubramanian *et al.* (2004). To achieve thin films on the pre-treated supports, the dip-coating method was applied. The third part of the chapter covers the performance evaluation conducted throughout this study. The process variables were; effect of catalyst loading, effect of initial phenol concentration, effect of solution pH, effect of UV wavelength and effect of H_2O_2 concentration. The final part is regarding the design of experiment used which is the RSM. This includes explanation of the ranges studied and the codes used as applied in the software.

Chapter Four consists of all the results and discussions related to the current research work. The first part of this chapter covers the characterization results obtained from SEM, EDX and XRD analyses of the immobilized Fe/TiO_2 thin film. The second part consists of a preliminary experiment involving the degradation of methylene blue in the batch reactor. This is followed by the third part, the determination of factors that influence photocatalytic activity where three sets of experiments were conducted. Then, the performance evaluation of the synthesized Fe/TiO_2 thin film by ways of evaluating the process variables are given in details. The effect of irradiation wavelength was also studied using three different irradiation sources which were UV-A, UV-C and visible light. In the fourth part, kinetics studies were performed on the degradation of phenol. The reaction order was determined using the rate law and the initial reaction rates method proved that phenol degradation follows the Langmuir-

Hinshelwood model. The final part for this chapter is regarding the optimization studies, completed by applying the Design of Experiment (DOE) method. A face-centered Central Composite design from the RSM was utilized to obtain the optimum values of the factors affecting the percentage of phenol degradation in this study.

The last chapter, Chapter Five gives the overall conclusion based on the results obtained throughout the current study as previously discussed in Chapter Four. It also includes several recommendations for future studies as a continuation for the present one.

CHAPTER TWO

LITERATURE REVIEW

This chapter presents the basic knowledge regarding wastewater treatments, photocatalysis processes, the selected photocatalyst; titanium dioxide, research related to the development of the photocatalyst and also research related to its performance and activity. An introduction to the design of experiment (DOE) regarding Response Surface Methodology (RSM) is also given.

2.1 PHENOL

Fresh water sources include rivers, lakes, wells and man-made reservoirs. In Malaysia, rivers are also a food source, even as a means of transportation. Unfortunately, as the population increases, as well as the increase in agriculture and industries, these fresh water sources have been compromised by pollutions. Nowadays, our water sources are heavily polluted with suspended, colloidal or dissolved impurities. With regards to pollution caused by the industry, the Environmental Protection Agency (EPA) in the United States of America has classified the pollutants into three groups; conventional, non-conventional and priority pollutants.

Phenol, listed in both the non-conventional and the priority list, can be classified as a dissolved pollutant where it is homogeneously dispersed in the liquid. According to the State of Ohio EPA, phenol is also a high priority PBT chemical. PBT chemicals, refer to persistent, bio-accumulative and toxic chemicals, non biodegradable, are not easily metabolized and may be hazardous to both human and the environment (State of Ohio EPA, 2002).

Phenol, chemical formula C_6H_5OH and chemical structure as shown in Figure 2.1, also refers to any compound which contains a six-membered aromatic ring, bonded directly to a hydroxyl group (-OH) (Wikipedia). It is used in a wide variety of applications; as a general disinfectant and in other medical compounds, drugs and pharmaceuticals, as a reagent in chemical analysis and in the manufacture of industrial organic compounds and dyes. It can also be found in the manufacture of fertilizers, explosives, paints and paint removers (Dept. of Environmental and Heritage, Australian Government, 2005).

Produced in large volume, phenol acts mostly as an intermediate in the production of other chemicals. The largest single use of phenol is as an intermediate in the production of low-cost and versatile phenolic resins and in thermoset resins used in plywood adhesive, construction, automotive, and appliance industries. It is also used as an intermediate in the production of caprolactam, which is used to make nylon and other synthetic fibres, and bisphenol A, which is used to make epoxy and other resins (Dept. of Environmental and Heritage, Australian Government, 2005; Kidak and Ince, 2006).

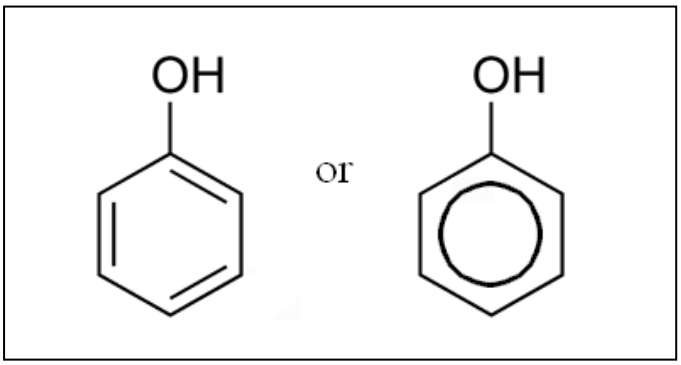

Figure 2.1: Chemical structure of phenol (Wikipedia).

Phenol can be found naturally in human and animal wastes, in some food, coal tar and in pine wood and pine needle. The synthetic phenol, which is toxic and difficult to degrade, can be obtained from the conversion of coal tar into gaseous or liquid fuels

and in the production of metallurgical coke from coal. It even exists as a component of oil refinery wastes. A more predominant way to mass produce phenol is through the decomposition of cumene hydroperoxide or prepared from either benzene sulphonic acid or chlorobenzene (State of Ohio EPA, 2002). It may enter the environment from oil refinery discharges, coal conversion plants, municipal waste treatment plant discharges, or spills (Dept. of Environmental and Heritage, Australian Government, 2005).

Phenol is a recalcitrant species in conventional wastewater treatment processes (Salaices *et al*., 2004) as it continues to form toxic solutions. Therefore phenol and its derivatives can act as a useful model contaminants for photocatalytic degradation research. This organic pollutant degrades through its hydroxylated compounds into carbon dioxide (CO_2) and water (H_2O) in the photocatalytic process. 1, 2, 4-trihydroxybenzene (1, 2, 4-THB), 1, 4-benzoquinone (1, 4-BQ) (Salaices *et al.*, 2004), hydroquinone and catechol (Brezova *et al*., 1997) are some of the intermediate species resulting from phenol degradation. Table 2.1 lists two types of industry that produces phenol at very high level concentration.

Table 2.1: Examples of pollutants' concentration in industrial wastewater. (Davis and Cornwell, 1998)

Industry	Pollutant	Concentration, ppm
Coke by-product (steel mill)	Ammonia	200
	Organic nitrogen	100
	Phenol	**2000**
Plywood-plant glue waste	COD	2000
	Phenol	**200-2000**
	Phosphorus	9 – 15

According to the Material Safety Data Sheet (MSDS, 2005) provided by Fisher Scientific, phenol may be fatal if inhaled, absorbed through the skin or swallowed. If inhaled at high concentration, phenol causes severe respiratory tract irritation with

possible burns. Direct contact with the skin would result in white, wrinkled discoloration of the skin followed by severe burns. It can also lead to severe digestive tract irritation with possible death due to respiratory failure when ingested. OSHA allowable limit or the permissible exposure limit (PEL) for phenol is 5 ppm.

Conventional wastewater treatments are as diverse as the impurities being treated in the wastewater. In fact, the treatment systems are divided into two where one system is used to treat municipal wastewater and the other is specifically for industrial wastes. The major goals of the three categories in municipal treatment system are to remove pollutants that will either settle or float, to remove soluble BOD_5 and finally to produce clean, colourless water. As for industrial waste, a more rigorous system is needed such as the Advanced Oxidation Processes (AOP).

For example, when air stripping method is used to remove volatile organic compounds (VOCs) in wastewater, the result is only the transfer of VOCs from liquid phase to air phase rather than destroying them. While for granular activated carbon (GAC) adsorption, the disposal of the spent carbon containing the adsorbed contaminant poses another problem. By utilizing AOP method, these problems can be avoided as this method promises complete mineralization of organic compounds into innocuous species, water and carbon dioxide (Chen and Ray, 1999).

2.2 PHOTOCATALYSIS

Photocatalysis is part of a group known as Advanced Oxidation Processes (AOP). The group can be categorized into three sub-group;

i) chemical oxidation using hydrogen peroxide (H_2O_2), ozone (O_3) and a combination of both, also known as HiPox technology,

ii) UV enhanced oxidation such as UV/ozone, UV/H_2O_2 and UV/TiO_2,

iii) wet air oxidation and catalytic wet air oxidation.

Such processes are able to produce a potent chemical oxidant known as hydroxyl radical (OH^+). According to Bolton *et al*. (1996), these important classes of technologies are capable of generating in situ hydroxyl radical, therefore accelerating the oxidation of a wide range of organic contaminants.

The work of Fujishima and Honda in 1968 had given birth to today's advanced photocatalysis. In their work, a single crystal TiO_2 electrode was irradiated and they successfully broke up water molecule into hydrogen and oxygen. Their work was actually focused on the production of hydrogen from water but it had resulted in the birth of photocatalysis. Several advantages offered by photocatalysis include:

a) complete mineralization of organic pollutants with the formation of CO_2, water and mineral acids,
b) photocatalytic process does not require the use of consumable reagents,
c) the irradiation required to activate the photocatalyst is in the near UV wavelength, making the use of solar irradiation a viable alternative. (Salaices *et al*., 2004)

As reported by Facchin *et al*. (2000), heterogeneous photocatalysis process depends on photon activation of a photocatalyst in mild experimental conditions i.e. at room temperature and atmospheric pressure. A solid with suitable surface physico-chemical and electronic properties can work efficiently as photocatalyst, depending on the reaction under investigation. The following items are essential in any photocatalytic process: a) a photocatalyst with efficient photon absorption; b) a high number of photo-reduced electron-hole pairs and c) a low recombination rate of these pairs. A favourite photocatalyst amongst researchers is titanium dioxide (TiO_2) and other existing photocatalysts are Fe_2O_3, CdS and ZnO (Wenhua *et al*., 2000; Arana *et al*., 2002).

2.3 REACTOR CONFIGURATION

Currently, two types of reactor exist for photocatalytic reactions. The first type is slurry reactor utilizing suspended or supported TiO_2 powder, while the other type is immobilized TiO_2 reactor. Reactor configuration plays important role in contributing to the efficiency of the photocatalyst's activity. Nevertheless, when it comes to reactor scale up for use in industry, slurry reactors are deemed a considerable challenge (Balasubramanian *et al*., 2004). Suspended photocatalyst would have to be filtered out after each treatment and this step requires additional filter configuration before the irradiated solution can be released (Grzechulska and Morawski, 2003). The depth of UV penetrating the irradiated solution is also a cause of concern since it can be limited by the strong absorption by catalyst particles and dissolved organic particles (Ray & Beenackers, 1998).

Therefore, researches have sought an alternative solution to these problems by using immobilized photocatalyst, thus avoiding the filtration problem. Unfortunately, the efficiency of immobilized reactors may be hindered by lower mass transfer area and the accessibility of photocatalyst surface to the reactants and photons. In actuality, problems exist in both uses of TiO_2 fine powders and supported TiO_2 fine powders. For TiO_2 fine powders, the problem is regarding its recovery after the reactions while for supported TiO_2, the activity becomes low due to the diminution of surface area (Yu *et al*., 2000). This phenomenon is further verified by Rachel *et al*. (2002) who reported that fixing TiO_2 on solid supports reduces its efficiency due to various reasons such as reduction of the active surface, difficult exchange within the solution including introduction of ionic species.

In this study, we used an annular batch reactor with a Pyrex/quartz glass tube acting both as a UV lamp shield as well as the support for TiO_2 thin film. According to Ray and Beenackers (1998), the distributive type annular reactors have a lot of scale

up potential. Their work stated that any reactor design with the photocatalyst fixed to substrates in the form of plates, rods or tubes inside the reactor will allow for high value of illuminated surface area of the photocatalyst.

2.4 TITANIUM DIOXIDE AS PHOTOCATALYST

Titanium, a metallic element, is known for its excellent corrosion resistance and when exposed to air, it forms a passive oxide, titanium dioxide (TiO_2). In the form of white powder pigment, TiO_2 has good covering power in many industrial applications such as paints, paper and plastics. Most importantly is the ability of TiO_2 to absorb UV light energy, utilized in photo-oxidation processes as a technique in wastewater treatment. Radiated TiO_2 produces pairs of electrical charges-holes in the valence band and electrons in the conductivity band. It has been reported that these holes will react with water molecules, forming hydroxyl radicals which are strong oxidants of the organic molecules (Trapalis *et al*., 2003). Table 2.2 lists examples of organic substances that can be degraded using TiO_2 photocatalysis.

Table 2.2: List of photocatalytic degradation of organic substrates using TiO_2. (Viswanathan, 2002)

Class	Examples of substances mineralized
Alkanes	Methane, isobutane, heptane, cyclohexane
Halo alkanes	Chloromethane, Br, Cl, F substituted ethane
Aliphatic alcohols	Methanol, ethanol, sucrose
Aliphatic carboxylic acid	Formic acid, propanicacid, oxalic acid
Alkenes	Propene, cyclohexene
Aromatic hydrocarbons	Benzene, naphathalene
Substituted aromatic hydrocarbons	Chlorobenzene, substituted nitrobenzene
Phenols and substituted phenols	Phenol, catechol, resorcinol, chlorophenols
Aromatic carboxylic acid	Benzoic acid, phthalic acid, salicylic acid
Polymers	Polyethylene
Dyes	Methylene blue, methyl orange
Pesticides	DDT, lindane, parathion

Recent photocatalysis researches are dominated by the use of TiO_2 since it is biologically and chemically inert, photoactively stable even when used for extended periods and readily available in the market (Ray, 1998; Mills *et al*., 2003). Table 2.3 lists some of the researches that utilized either commercial TiO_2 or some other moderation. Operated at ambient temperature (reaction temperature usually ranges from 30°C to 35°C), this process also offers possible utilization of solar energy (visible light, $\lambda > 450$) for photocatalytic oxidation reactions (Guillard *et al*., 2002). This possibility has been studied extensively in the effort to enhance TiO_2 absorption capability by adding dopants. Further discussion regarding research on doped TiO_2 is presented in Section 2.5.2.

Table 2.3: Types of TiO_2 used in the degradation of organic contaminant.

Research done by	**Organic contaminant**	**Type of TiO_2 photocatalyst**	
		Commercial	**Own work**
Piscopo *et al.* (2001)	Benzamide solution	Degussa P25	TiO_2/SG
Chen and Ray (2001)	Toxic metal ions	Degussa P25 & Hombikat UV100	-
Rachel *et al.* (2002)	3-NBSA and 4-NTSA	Degussa P25	TiO_2 coated on various support
Villacres *et al*. (2003)	2-propanol	-	Coated P25
Grzechulska and Morawski (2003)	Phenol	-	Coated P25
Ksibi *et al.* (2003)	Substituted phenols	Degussa P25	-
Salaices *et al*. (2004)	Phenol	Degussa P25 & Hombikat UV100	-
Kabir *et al*. (2006)	Phenol	-	Degussa P25 & silica zeolite attached to glass beads

TiO_2 exists as three naturally occurring minerals; anatase, rutile and brookite, also known as polymorphs. These polymorphs have many applications, for example as photocatalyst, photoelectrodes, gas sensors and electrochromic display devices (Miah *et al*., 2000). However, in photocatalysis, the anatase crystalline phase is preferred for its stable photoactivity and prolonged lifetime. The band spacing of the anatase

modification of Eg = 3.2 eV, including high oxidation potential of its valence band of Eg = 3.1 eV makes it possible to oxidize virtually any organic molecule under UV radiation (wavelength < 390 nm) (Trapalis *et al.,* 2003). When TiO_2 is irradiated by UV light, with energy greater than the bandgap energy of the photocatalyst, it adsorbs photon from the light, thus electron-hole pairs are generated within the photocatalyst, expressed in Equation 2.1:

$$TiO_2 + hv \longrightarrow h^+ + e^- \qquad (2.1)$$

The hole (h^+), reacts with H_2O molecule and adsorbed hydroxide ions (OH^-) in an oxidative reaction to produce hydroxyl radical ($OH^\bullet$). The photooxidative radical will then degrades the organic pollutant in the water. These reactions can be written as shown in Equations 2.2 to 2.5:

$$h^+ + OH^- \longrightarrow OH^\bullet \qquad (2.2)$$

$$h^+ + H_2O \longrightarrow OH^\bullet + H^+ \qquad (2.3)$$

$$h^+ + P_{ads} \longrightarrow P^+_{ads} \qquad (2.4)$$

$$OH^\bullet + P_{ads} \longrightarrow P_{oxid} + H_2O + CO_2 \qquad (2.5)$$

where P_{ads} represents the organic pollutant adsorbed on the catalyst surface. The electron (e^-) reacts in a reductive reaction with dissolved O_2, as shown in Equation 2.6:

$$e^- + O_2 \longrightarrow O_2^- \qquad (2.6)$$

Apparently there is one disadvantage when utilizing TiO_2 as photocatalyst; its bandgap energy of 3.2 eV requires UV illumination to activate it (Trapalis *et al*., 2003). TiO_2 only absorbs about 3 – 5 % energy of the solar spectrum which reaches the earth at wavelength of 400 – 800 nm (Anpo, 2000; Sonawane *et al*., 2004). Therefore, this absorption edge needs to be extended to the visible range if the photocatalyst is to be used in applications which involve direct sunlight. So far, bandgap narrowing by using dopant is one of the most investigated methods to achieve this goal.

2.5 SYNTHESIS AND IMMOBILIZATION METHOD FOR THIN FILMS

In this study, Fe doped TiO_2 was synthesized using the sol gel method reported by Balasubramanian *et al*., (2003). The sol gel was immobilized onto a support (Pyrex or quartz glass tube) by using the dip-coating method. The coated support was then used in the batch reactor. By immobilizing the photocatalyst onto glass tubes, separation or filtration process can be eliminated. The sol gel method, as reported by Balasubramanian *et al.* (2003), produces a stable sol which can be used even after a few months in storage. No physical changes were detected of the stored sol.

They claimed that for each dip-coating/heating cycle on a stainless steel substrate, they obtained uniform films with thickness of 3 – 4 μm and it increases fairly linearly. Furthermore, by testing the films' hardness using the pencil hardness method, they discovered that a relatively soft film yet with very good adherence was formed. The immobilized TiO_2 photocatalyst was then tested in a batch reactor for the degradation of 4-chlorobenzoic acid (Balasubramanian *et al.,* 2004). The result showed that the activity of the photocatalyst increases with the number of coating cycles, from 1 coat up to 3 coats but the activity tapers of after 4 coats. At this thickness, UV radiation was blocked and the photons were unable to further activate the photocatalyst. Apart from that, the dip-coating method was chosen firstly due to the availability of the Dip-Coating Apparatus, secondly because it allows for easy handling of the chosen substrates.

2.5.1 SOL-GEL METHOD

According to Mills *et al.* (2003), other methods of preparing TiO_2 thin films include chemical vapour deposition (CVD), sputtering and thermal oxidation. However, they claim that sol gel method is the simplest and most popular method. Using sol gel route to synthesize TiO_2 is advantageous, as no special equipment other than a

furnace is needed. Plus, the film properties can be determined by controlling sol preparation parameters such as concentration and nature of precursors, viscosity, withdrawal speed, temperature and the duration of heat treatment (Balasubramanian *et al*., 2003). Our interest in sol gel is due to its easy application, both during synthesis as well as during dip-coating of the thin film onto the support.

In other research studying the viability of immobilized photocatalyst, sol gel method is also the preferred method (Mills *et al*., 2003; Balasubramanian *et al*., 2004; Tseng *et al*., 2004 and Sonawane *et al*., 2004). It is basically the result of mixing three main ingredients; titanium precursor, organic solvent and stabilizer or additive. Depending on the desired properties, these main components can be changed. Guillard *et al*. (2002) synthesized different sol-gel solutions and coated them on silicon wafers, soda lime glass and Pyrex plates using dip-coating technique, as listed in Table 2.4. Different mixtures were reported to produce varying results, in this case, different thickness.

Table 2.4: Different sol-gel methods. (Guillard *et al*., 2002)

Precursor	**Solvent**	**Stabilizing agent**	**Additives**	**Thickness (μm)**
TTIP	Isopropanol	-	-	0.65
TTIP	Isopropanol	Acetic acid	-	0.25
TTIP	Isopropanol	Acetyl acetone	Water	0.21
TTIP	Butanol	-	Water, HNO_3.6N	0.23
TET	Ethanol	Acetic acid	Water	0.15

TTIP: titanium tetraisopropoxide; TET: titanium ethoxide; thickness was measured using profilometer.

The sol-gel procedure used in this study includes titanium isopropoxide as the titanium precursor, isopropanol as the solvent and diethanolamine (DEA) as the stabilizing agent. In an investigation concerning the solvent effect of the hydrolysis of metal alkoxide, it was found that glycols or ethanolamines can suppress the precipitation of the oxides from the alcoholic solution of metal oxide (Takahashi and Matsuoka, 1988). Ferric nitrate with chemical formula $Fe(NO_3)_3.9H_2O$ is the source of Fe dopant. Other research employing the use of ferric nitrate as dopant includes Yang *et al*. (2002), Trapalis *et al*. (2003) and Sonawane *et al*. (2004). The procedure is given in detail in Chapter 3.

Another advantage of applying sol-gel technique is the heat treatment. By controlling the calcination temperature, researchers can produce two types of TiO_2 crystalline form. One is the rutile phase, used mostly in paints and pigments due to its scattering effect against ultraviolet light (Kim *et al*., 2004). While the anatase phase, possessing the bandgap energy of 3.2 eV is required for photocatalysis. According to Robert *et al*. (1999), the thermal treatment and its duration can influence the formation of TiO_2 crystal. They proposed that the best temperature treatment is at 400 - 500°C, for 15 – 20 hours, necessary to obtain TiO_2 anatase phase.

This is because the anatase crystalline form is the most efficient form for photocatalysis (Guillard *et al*., 2002; Sonawane *et al*., 2004). Figure 2.2 shows the disappearance rate of malic acid using TiO_2 thin films prepared at different calcination temperatures (Guillard *et al*., 2002). The figure shows increasing rate of malic acid disappearance when the calcinations temperature was increased. Maximum disappearance rate was achieved at calcinations temperature of 400˚C. They concluded that crystallised anatase phase was responsible for the observed result.

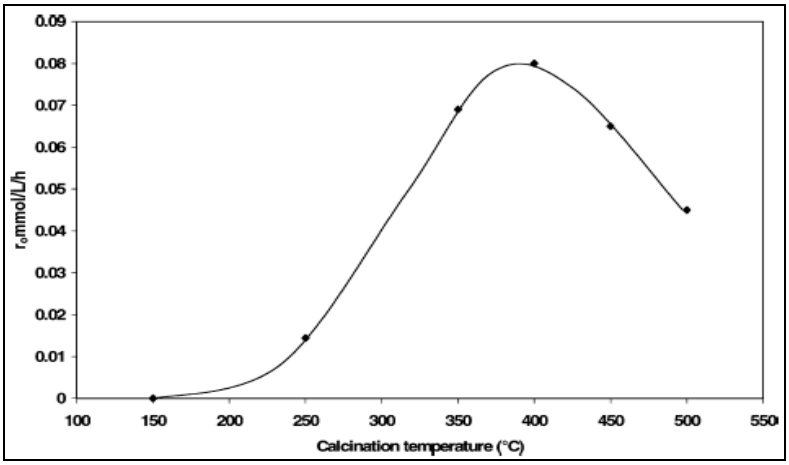

Figure 2.2: Disappearance rate of malic acid as a function of calcination temperature. (Guillard *et al*., 2002)

While the XRD patterns for different calcinations temperature is shown in Figure 2.3 indicating a high prominent appearance of anatase phase when the temperature was increased (Jiang and Gao, 2002). Higher anatase peak was observed for 10% Fe doped powder calcined at 500˚C with comparison to the powder calcined at 450˚C. These results confirmed that temperature affects the formation of TiO_2 crystal phases.

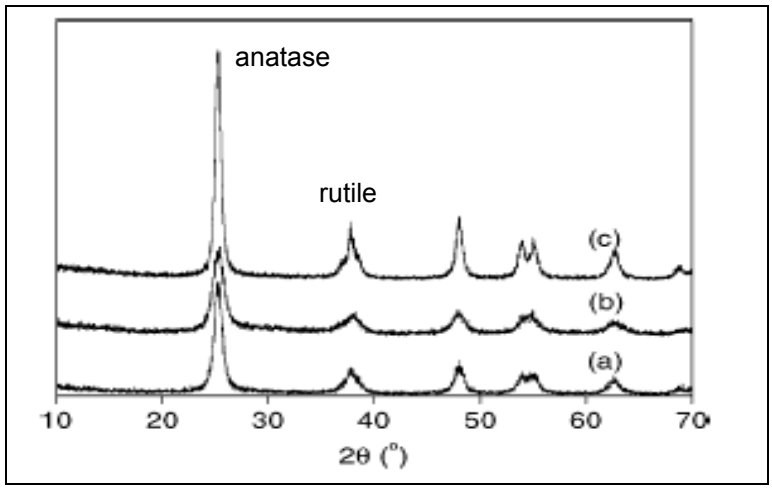

Figure 2.3: XRD patterns showing anatase and rutile peaks at different temperatures. (a)TiO_2 (450°C); (b) 10 mol% Fe doped powders (450°C); (c) 10mol% Fe doped powders (500°C). (Jiang and Gao, 2002)

2.5.2 TRANSITION METAL ION AS DOPANT

In the Periodic Table, the elements that correspond to the d level fillings (3d orbitals filling) are called d block elements. A transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. They also have a wide range of oxidation states. As stated in Chapter 1, TiO_2 sol gel doped with Fe^{3+} has been synthesized to study its activity in UV and solar light.

Rajeshwar *et al*. (2001) concluded that there are three main consequences of metal-modification of TiO_2:

a) stimulation of visible light photoresponce in the host material
b) suppression (or in some cases, enhancement) of electron-hole recombination as a result of new states introduced in the band-gap of TiO_2 by these dopants
c) generation of catalytic sites on the TiO_2 surface that serve to store electrons for subsequent transfer to acceptor species in the solution.

Yang *et al*. (2002) further added that transition metal ions used as dopants are able to enhance the attachments of the functionalized organic pollutants to the doping ion active sites. Jiang and Gao (2002) and Sonawane *et al.* (2004) reported that using Fe^{3+} as dopant has increased TiO_2's photocatalytic activity due to the shift in optical absorption, also known as the red shift. They discovered that TiO_2 doped with Fe^{3+} were able to absorb both UV and a portion of the visible range (the longer wavelength), causing the shift. Figure 2.4 clearly shows the result of the red shift as presented by Jiang and Gao (2002).

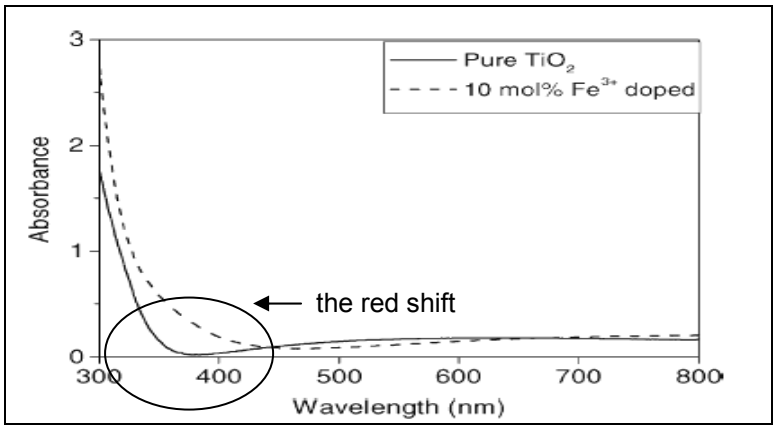

Figure 2.4: UV-Vis absorption spectra of pure and doped thin films.
(Jiang and Gao, 2002)

Sonawane *et al.* (2004) proposed that photodegradation of organic compounds using Fe/TiO_2 occurs when the photocatalyst is illuminated with sunlight in the presence of water containing dissolved oxygen and organic contaminants. The organic contaminants are decomposed to CO_2 and H_2O under these conditions, as shown in Equations 2.7 to 2.10:

$$Fe/TiO_2 \xrightarrow{hv} Fe/TiO_2\,(e^- + h^+) \qquad (2.7)$$

$$h^+ + OH^- \longrightarrow OH^\bullet \qquad (2.8)$$

$$h^+ + H_2O \longrightarrow OH^\bullet + H^+ \qquad (2.9)$$

$$e^- + O_2 \longrightarrow O_2^- \qquad (2.10)$$

The hydroxyl radicals will then attack the organic contaminant as previously discussed in Section 2.4.

Jin and Shiraishi (2004) reported that the presence of metal ions attracts positively-charged holes, thus inhibiting its recombination with electrons (in agreement with Rajeshwar *et al*., 2001). This phenomenon in turn, increases the formation of hydroxyl radical which controls the decomposition rate in an aqueous solution. While Facchin *et al*. (2000) states that the rate of a photo-oxidation reaction depends on the charge transfer process occurring from TiO_2 to the dissolved O_2. The presence of

transition metal ions on the surface of the photocatalyst particles improves the rate of electron transfer to O_2 (Equation 2.10) and consequently has a beneficial effect on the photo-oxidation rate of organic species.

Nonetheless, Anpo (2000) disagreed and stated that these dopants exist only as the recombination centre for the electron/holes, thus having no noticeable effect on the reaction rate. This statement was also in agreement with Brezova *et al*. (1997).

2.5.3 DIP COATING METHOD

Historically, the physical dimension of thickness was used to differentiate thick films and thin films. Unfortunately, the critical thickness value depends on the application and discipline. In recent years, a “Confucian” solution has been advanced. It states that if a coating is used for surface properties such as electron emission or photocatalytic activity, it is a thin film. Whereas if it is used for bulk properties such as corrosion resistance, then it can be identified as thick film. Thus, the same coating material of identical thickness can be a thin film or a thick film depending upon the usage (Bunshah, 1994).

As stated in Section 1.2, the synthesized sol-gel was coated on Pyrex and quartz glass tubes using dip coating, also known as wet coating method. Dip coating is a method of immersing the substrate in a liquid, in this case the sol-gel, and then withdrawn at a preset speed (Schmidt and Mennig, 2000). The coated substrate is then put through heat treatment to obtain a ‘glass-like’ material on its surface. Depending on the desired thickness of the thin film, this whole process is repeated until the desired thickness is acquired. Apart from that, the film thickness can also be controlled by changing the viscosity of the sol-gel. Dip coating allows easier handling of different substrates which give reason to why many researchers applied this method in their work, as shown in Table 2.5.